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Heat capacity and thermodynamic properties of ethyl carbazate ($C_3H_8N_2O_2$)

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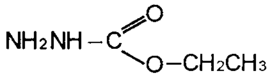
Abstract

The low temperature heat capacities of ethyl carbazate ($C_3H_8N_2O_2$) were precisely determined with an adiabatic calorimeter over the temperature range from 78 to 371 K. The sample was observed to melt at 318.92 ± 0.02 K. The molar enthalpy and entropy of the melting as well as the chemical purity of the substance were determined to be 20019 ± 11 J mol^{-1}, 62.77 ± 0.03 J mol^{-1} K^{-1} and 99.35 ± 0.01 mol%, respectively. The extrapolated melting temperature for the absolutely pure compound obtained from fractional melting experiments was 319.181 ± 0.005 K. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ethyl carbazate; Heat capacity; Adiabatic calorimetry; Purity determination

1. Introduction

Ethyl carbazate (molecular formula: $C_3H_8N_2O_2$; CA registry no.: 4114-31-2) is an important raw material and intermediate, which has been widely used in the syntheses of many medicines, herbicides, growth regulator of plant, germicides and insecticides. Ethyl carbazate has been used to prepare various Schiff base metal complexes [1] with excellent antibiotic and anticarcinogenic activity. Recently, it has been considered as an energy-storage material for aircrafts due to its high enthalpy of fusion, noncorrosiveness, nontoxicity and good thermal stability. Its molecular structure is



In 1914, Diels [2] used hydrazine and diethyl carbonates as reactants and successfully synthesized the compound at room temperature. He reported that the melting point and boiling point of the compound were 45–47 and 108–109°C, respectively. Since then, no reports on the thermodynamic properties of the substance have been reported. For the application of the compound, thermodynamic data for this substance is required. In the present work, low temperature heat capacity measurements were carried out with adiabatic calorimetry, and the basic thermodynamic parameters, such as molar enthalpy and entropy of melting has been determined. The chemical purity of the

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substance was determined by fractional melting experiments.

2. Experimental

2.1. Sample preparation and characterization

Ethyl carbazate ($C_3H_8N_2O_2$) is a colorless and transparent crystal with a lumpy crystalline shape. The sample used for the present calorimetric study was supplied from the pesticides institute of Northwest University, China. It was prepared according to the procedures given in literature [2], in which 85% hydrazine hydrate and diethyl carbonates were used as the reactants. The crude product was purified by column chromatography in which the chloroform was used as the eluant. The melting point of the final product was determined to be 45.1–46.5°C with a microscopic melting point device (model: BY-1, Yazawa co., Japan), in agreement with literature [2]. ^{1}H NMR (model: Unity Plus 500, made by Varian Ltd., USA, $CDCl_3$) absorption peaks were detected at $\delta = 1.33$ (m, 3H, CH_3), 3.92 (m, 2H, CH_3), 4.24 (m, 2H, NH_2) and 6.93 (m, H, NH) ppm. IR (model: 260-10, made by HITACHI, Japan) showed characteristic absorption peaks at 3331, 2938, 1704, 1641, 1492, 1281, 1178 and 1063 cm^{-1}. These results were identical with those of the literature [3]. Its actual purity was determined by HPLC (model: LC-10AT, Shimadzu, Japan) analysis to be higher than 99.35 mol%.

2.2. Adiabatic calorimetry

The heat capacity measurements were made by an adiabatic calorimetric system for small samples over the temperature range from 78 to 371 K. The construction of the calorimeter has been described previously in detail in [4,6]. It consists of a sample cell, a thermometer, a heater, two (inner and outer) adiabatic shields, differential thermocouples, a vacuum can and a Dewar vessel. Liquid nitrogen was used as the cooling medium. The evacuated can or chamber was kept within 10^{-3} Pa vacuum in the temperature range of 78–371 K to eliminate the heat loss owing to the gas convection, and a small amount of helium gas was introduced through a length of copper capillary at the center of the upper cover into the cell to improve the heat transfer of the whole sample cell. The sample cell was sealed with the tin solder after the copper capillary was pinched off from the tube end. Two adiabatic shields surrounded the sample cell in turn and a vacuum can was immersed in liquid nitrogen. The two adiabatic shields were made of chromium-plated copper and equipped with manganin heating wires. Two sets of six-junction chromel-contantan (Ni 55%, Cu 45%) thermocouples were used to measure the temperature differences between the sample cell and the inner adiabatic shield and between the inner and the outer adiabatic shields. The temperatures of the two shields were controlled separately and automatically with two units of auto-adiabatic controller. When the temperature in the sample cell increases due to heating, the thermocouples measure the temperature differences. This signal is used to control the heaters distributed on the walls of the inner and outer shields, respectively. Both shields were heated under the control of the signal and kept at the same temperatures as that of the sample cell. In this way, the heat loss caused by the radiation is greatly reduced.

The sample was heated using the standard discrete heating method and the temperature of the sample was alternatively measured. The heating time was 10 min, the equilibrium time of every experimental point is 5 min, and the temperature drift rates of the sample cell measured in an equilibrium period were usually within 10^{-4}–10^{-5} K min^{-1}. During the heat capacity measurements, the temperature difference between the inner adiabatic shield and the sample cell was automatically kept within 10^{-3}–10^{-4} K in order to obtain a satisfactory adiabatic condition. The data of heat capacities and corresponding equilibrium temperatures were corrected for heat loss [4,6].

The mass of the sample loaded in the sample cell amounted to 4.1402 g, which was equivalent to 0.03977 mol based on its molar mass of 104.1085 g mol^{-1}.

The molar heat capacities of α-Al_2O_3 used as the standard substance were measured in the same temperature range as that of the sample measurement in order to confirm the reliability of the calorimeter. The sample mass used for the measurements was 1.8219 g, which was equivalent to 0.0179 mol based on its molar mass, $M\ (Al_2O_3) = 101.9613$ g mol^{-1}. Deviations of the experimental results from those of the smoothed curve lie within ±0.2%, while the inaccuracy is within

Table 1
Experimental molar heat capacities of ethyl carbazate obtained from first series of repeated measurements ($M = 104.1085$ g mol^{-1})

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})
78.592	58.84	209.463	119.31	318.425	10077
80.527	60.40	212.708	120.88	318.472	12066
82.469	61.49	215.890	122.24	318.514	12991
84.343	62.82	219.094	123.60	318.549	14010
86.182	63.96	222.213	124.96	318.581	15795
87.988	65.30	225.290	126.39	318.612	17003
89.763	66.46	228.367	127.85	318.642	17997
91.515	67.38	231.380	129.04	318.669	18700
93.243	68.66	234.394	130.46	318.697	19495
95.256	69.88	237.408	132.09	318.720	20550
97.549	71.07	240.316	133.59	318.745	21422
99.785	72.19	243.330	134.80	318.768	22171
102.001	73.41	246.217	136.07	318.789	23196
104.158	74.40	249.125	137.54	318.815	24220
106.299	75.41	252.034	138.99	318.838	25413
108.407	76.51	254.953	140.53	318.859	26835
110.497	77.72	257.890	142.26	318.884	28670
112.537	78.85	260.680	144.01	318.905	30917
114.763	80.11	263.410	145.47	318.928	34878
117.162	81.12	266.255	147.13	318.949	40396
119.517	82.36	268.987	148.75	318.967	33411
121.827	83.44	271.699	151.21	318.991	24586
124.137	84.68	274.424	152.77	319.017	19182
126.379	85.68	277.208	155.01	319.119	3606.8
128.639	86.71	279.834	156.76	320.131	216.93
130.881	87.92	282.466	158.99	322.002	219.31
133.106	88.79	285.210	161.65	323.945	221.56
135.214	89.94	287.865	164.54	325.799	224.06
137.423	90.96	290.344	166.70	327.747	227.10
139.530	92.09	292.910	169.86	329.579	230.37
142.156	93.24	295.345	172.71	331.549	234.12
145.342	94.39	297.734	175.69	333.380	236.92
148.455	95.79	300.213	179.27	335.328	241.06
151.568	96.88	302.603	183.12	337.182	244.25
154.504	98.02	304.816	186.84	339.037	247.61
157.572	99.06	307.028	190.69	340.984	251.66
160.582	100.37	309.153	193.99	342.839	255.79
163.488	101.37	311.056	197.89	344.670	258.99
166.453	102.40	312.782	201.84	346.525	262.27
169.300	103.35	314.198	205.87	348.379	265.39
172.133	104.31	315.333	210.89	350.257	269.28
174.980	105.06	316.172	230.42	352.089	273.34
177.709	105.92	316.775	406.70	353.943	276.54
180.394	106.84	317.167	1544.3	355.705	280.28
183.241	107.85	317.436	2341.9	357.559	283.63
186.027	109.08	317.647	3091.0	359.321	286.36
188.704	110.26	317.799	3712.9	361.176	290.89
191.380	111.43	317.938	4385.8	362.938	295.33
194.036	112.58	318.056	5017.0	364.792	299.00
196.670	113.85	318.151	5791.2	366.554	302.66
199.684	115.21	318.235	6463.1	368.409	307.96
202.972	116.50	318.306	7400.6	370.078	311.78
206.259	117.86	318.369	8699.5		

±0.5%, as compared with those of the National Bureau of Standards [5] over the whole temperature range.

3. Results and discussion

3.1. Heat capacity

All heat capacity measurements are listed in Table 1 and plotted in Fig. 1. The structure of the compound is stable: no phase change occurred in the solid phase, nor did association or decomposition occur in the liquid phase ($T < 371$ K).

The experimental values of the heat capacities have been fitted to polynomial equations by the least square method.

For the solid phase

$$\begin{aligned} C_{\mathrm{p,m}}\,(\mathrm{JK^{-1}\,mol^{-1}}) = {} & 113.7823 + 48.6060X \\ & + 11.8001X^2 + 1.0387X^3 \\ & - 18.9211X^4 + 24.3393X^5 \\ & + 26.4327X^6 \end{aligned}$$

in which $X = [(T\,(\mathrm{K})) - 196.5]/118.5$. The above equation is valid from 78 to 315 K, with an uncertainty of ±0.25%.

For the liquid phase

$$\begin{aligned} C_{\mathrm{p,m}}\,(\mathrm{JK^{-1}\,mol^{-1}}) = {} & 259.7857 + 48.8361X \\ & + 4.6000X^2 \end{aligned}$$

in which $X = [(T\,(\mathrm{K})) - 345.5]/25.5$. This equation applies to the range from 320 to 371 K, with an uncertainty of ±0.20%.

3.2. Melting point, enthalpy and entropy of fusion

Pre-melting occurred owing to the presence of impurities in the sample. The measurement of the melting point and the molar enthalpy of fusion of the sample was done as follows: first, the temperatures for the start of the pre-melting and for complete melting were determined. Between these two temperatures, the melting point was determined by successive approximation through stepwise heating. Then, by heating the

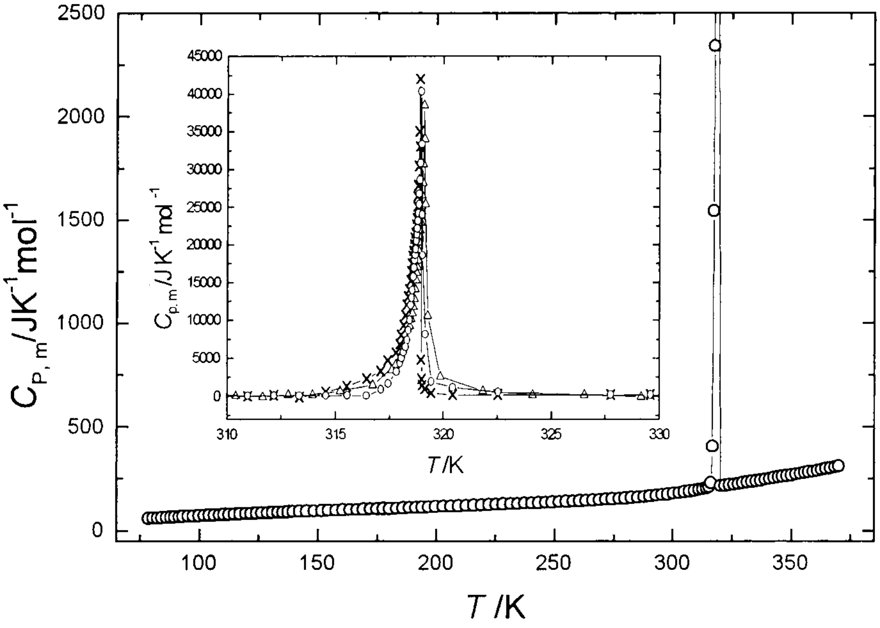

Fig. 1. Experimental molar heat capacities $C_{\mathrm{p,m}}$ of ethyl carbazate ($C_3H_8N_2O_2$) obtained by adiabatic calorimetry. "○" represents the first series of heat capacity measurements; "△", the second series of heat capacity measurements; "×", the third series of heat capacity measurements.

Table 2
The results of phase transition obtained from three series of repeated experiments of ethyl carbazate ($C_3H_8N_2O_2$)

Thermodynamic properties	Series 1 x_i	Series 2 x_i	Series 3 x_i	Mean value $\bar{x}$	Standard deviation σ_a [a]
T_{fus} (K)	318.93	318.93	318.88	318.92	0.02
$\Delta_{fus}H_m$ (J mol^{-1})	20012	20040	20004	20019	11
$\Delta_{fus}S_m$ (J K^{-1} mol^{-1})	62.75	62.83	62.73	62.77	0.03
T_0 (K)	319.176	319.191	319.175	319.181	0.005
T_1 (K)	318.905	318.921	318.902	318.909	0.007
(1−N) (%)	99.36	99.36	99.34	99.35	0.01

[a] $\sigma_a = \sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2/n(n-1)}$, in which n is experimental number ($n = 3$); x_i, experimental value of each series of repeated measurement; $\bar{x}$, mean value.

sample from a temperature slightly lower than the initial melting temperature to a temperature slightly higher than the final melting temperature, the enthalpy of fusion of the sample was evaluated. The enthalpy used to heat the empty sample container and the sample was subtracted from the total amount of heat introduced to the sample and container during the whole fusion [6].

Three series of heat capacity experiments in the fusion region of the compound were carried out so that the reversibility and repeatability of the fusion region were verified. Before these series, the sample was cooled from 371 K to lower than 293 K using different cooling rates. In the first series, the sample was quenched into liquid nitrogen (about 20 K min^{-1}), in the second series, the sample was naturally cooled (about 0.5 K min^{-1}), and in the third series, the ice-water was used as coolant (about 5 K min^{-1}). The results of the three series of repeated experiments are plotted in the inset to Fig. 1 and also given in Table 2. It can be seen from Fig. 1 that the phase transition is reversible and repeatable, no supercooling and no other thermal anomaly was caused by the different cooling rates.

The melting temperature, T_{fus} of the sample was calculated from an equation based on the heat capacity in the fusion region, as described in the literature [6,7]. The molar enthalpy of fusion $\Delta_{fus}H_m$ was determined in accordance with a method introduced in the literature [7–9]. The molar entropy of fusion $\Delta_{fus}S_m$ was derived from the molar enthalpy of fusion, using $\Delta_{fus}S_m = \Delta_{fus}H_m/T_{fus}$ [7–9].

The results of T_{fus}, $\Delta_{fus}H_m$ and $\Delta_{fus}S_m$ obtained from the three series of repeated heat capacity measurements are listed in Table 2.

3.3. Purity determination of the sample

The purity of the sample is evaluated from a set of equilibrium melting temperatures (T) and melting fractions (F) corresponding to these temperatures [8,9]. The experimental results obtained from the heat capacity measurements in the fusion region are listed in Table 3. The equilibrium melting temperature (T)

Table 3
Experimental results of melting fractions (F) and equilibrium temperature (T) of ethyl carbazate ($C_3H_8N_2O_2$)[a]

T (K)	F	$1/F$
Series 1		
316.775	0.1126	8.8819
317.647	0.1755	5.6973
318.056	0.2455	4.0752
318.369	0.3531	2.8323
318.549	0.4360	2.2937
318.669	0.5400	1.8518
318.768	0.6343	1.5767
318.859	0.7909	1.2644
Series 2		
317.798	0.1932	5.1765
318.110	0.2512	3.9806
318.496	0.3919	2.5518
318.716	0.5679	1.7606
318.839	0.7376	1.3558
Series 3		
317.429	0.1572	6.3608
318.150	0.2678	3.7344
318.373	0.3445	2.9030
318.634	0.5208	1.9202
318.768	0.6958	1.4372

[a] $F = q/(\Delta_{fus}H_m n)$, in which q is the amount of heat introduced to melt the sample for the melting fraction F; n the mole number of the sample.

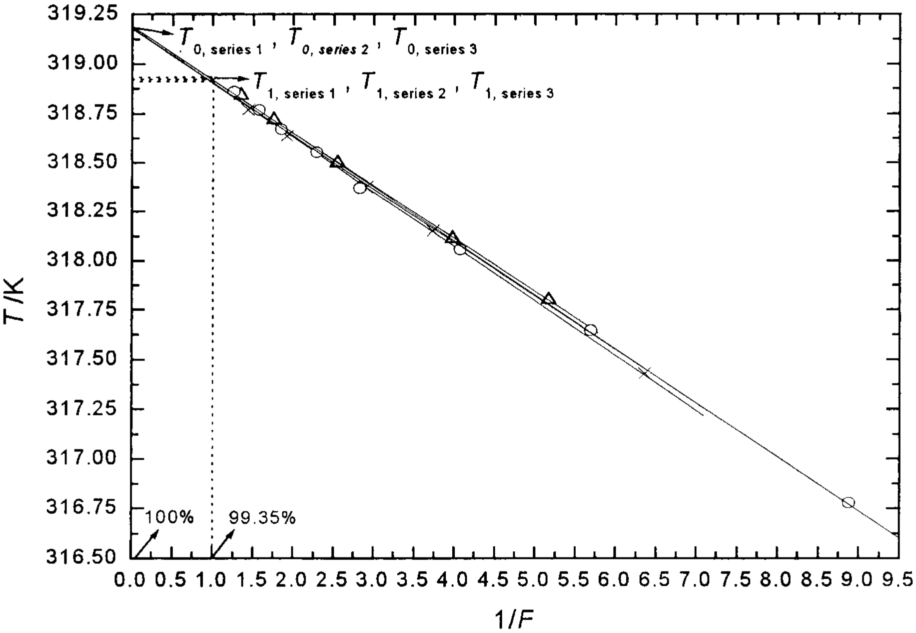

Fig. 2. The equilibrium temperature (T) vs. the reciprocal of the melting fractions ($1/F$) for ethyl carbazate ($C_3H_8N_2O_2$) during fusion. The symbols are explained in Fig. 1.

versus the reciprocal of the melting fractions ($1/F$) is a straight line, as shown in Fig. 2. Extrapolation of the straight line to $1/F = 0$ and $1/F = 1$ gives T_0 and T_1 for each series of experiment, respectively, as indicated in Table 2. Here, T_1 is the melting temperature of the impure compound obtained from fractional fusion experiments and T_0 is the melting point of a theoretically or absolutely pure sample. The melting point ($T_1 = 318.909 \pm 0.007$ K) obtained from the fractional melting agrees well with that ($T_{\mathrm{fus}} = 318.92 \pm 0.02$ K) obtained from the heat capacity measurements as described above. The mole percentage (N) of impurities in the sample is obtained from the Van't Hoff equation [9]. The purity of the sample ($1-N$) is 99.35 ± 0.01 mol%, in agreement with the result of chromatographic analysis (99.35 mol%).

Acknowledgements

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